PATENT SPECIFICATION

836,026

NO DRAWINGS.

Date of filing Complete Specification: Aug. 15, 1957.

Application Date: Aug. 15, 1956. No. 24990/56.
(Patent of Addition to No. 813,801, dated Sept. 15, 1954).

Complete Specification Published: June 1, 1960.

Index at Acceptance:—

Classes 72, A(8:11D); and 82(1), A8(A2:A3:K:M:Q:R:U:W:Z2:Z5:Z8:Z12), A15A.

International Classification:—C21d. C22c.

COMPLETE SPECIFICATION.

Improvements in or relating to Martensitic Stainless Steels.

We, JOHN IVAN MORLEY, a British Subject, of 175 Hemsworth Road, Norton, Sheffield 8, Yorkshire, CHARLES SYKES, F.R.S., a British Subject, of Atlas & Norfolk Works, Sheffield 1, Yorkshire, and ROBERT MOWBRAY NORRIS GRAY, a British Subject, of 10 Whirlow Park Road, Sheffield 11, Yorkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to martensitic stainless steels possessing superior corrosion resistance.

Our earlier Patent Specification No. 813,801 describes and claims corrosion-resistant martensitic stainless steel characterised by a composition consisting of 0.03 to 0.15% carbon plus nitrogen (with total nitrogen not exceeding 0.05%) over 15% and up to 17.5% chromium, 4 to 6.5% nickel, 0.5 to 2.5% copper, 0.3 to 3.0% molybdenum, 1% maximum silicon, 1% maximum mang nese together with one of the following carbide or nitride forming elements: niobium (including any residual tantalum) in amount between 8 and 12 times the carbon plus nitrogen content, titanium or vanadium in similar proportions whichever is used, amounting to 5 to 10 times the carbon plus nitrogen content and the remainder iron and any incidental impurities such as any aluminium introduced incidentally as an impurity in the ferro alloys and small residual amounts of elements such as sulphur and phosphorus that are associated with steel melting processes.

Although steels within the above composition ranges may be hardened by heat treatment to give high proof stress and high tensile strength coupled with excellent corrosion resistance, they are not ideally suited to the production of flat rolled products by cold rolling, because individual casts vary in the degree of softening that may be achieved by air cooling the steels from about 1050° C. In some casts considerable amounts of austenite are retained by air cooling thin sections less than about $\frac{1}{16}$" thick from 1050° C. and the resulting yield points may be about 20 tons/sq. in. Such material may be fairly readily cold rolled to thin sheet or cold formed in the manufacture of components from sheet. Other casts, however, retain very little austenite after air cooling from 1050° C., and become martensitic after this treatment, with the result that they are hard and difficult to cold work. In both cases, however, the steels will respond to the subsequent hardening treatments described in the said Application.

The present invention is an improvement in or modification of the steels according to the above-mentioned Patent Application.

In its broadest aspect, the present invention provides highly corrosion-resistant martensitic steel which is an improvement in or modification of the composition according to Patent Specification No. 813,801 and comprises: 0.03 to 0.12% carbon plus nitrogen (with total nitrogen not exceeding 0.03%), over 13.5 and up to 17.5% chromium, 4.0 to 6.0% nickel, 0.5 to 2.5% copper, 0.3 to 3.0% molybdenum, 0.5 to 2.5% manganese, 1% maximum silicon, and 0 to 0.2% preferably at least 0.03%, of any one or more of the following carbide and nitride forming elements, titanium, vanadium, and niobium, and the remainder iron except for any aluminium introduced as an impurity in the ferro alloys, small residual amounts of elements

such as sulphur and phosphorus associated with steel melting processes.

Steels according to the invention may be produced as castings, or as forgings, stampings, plates or bar by hot-rolling, or as cold-rolled sheet, strip, foil or cold-drawn wire, and may be heat-treated to a high tensile strength in a similar manner to that described in the main Application.

A preferred composition embodying the invention contains carbon not more than 0.06%, chromium 15% to 17%, nickel 5% to 6%, copper 1% to 2.5%, molybdenum 1.5% to 2.5% and titanium 0.03% to 0.12%.

The invention enables steels to be provided capable of being fully heat treated to develop mechanical properties and corrosion resistance similar to those according to the above-mentioned earlier Application and which by virtue of the modified composition are capable of developing more consistently a soft low yield point condition as the result of an intermediate heat treatment, this property being advantageous in the production of sheet, strip, foil and wire rod or coil by the customary methods of cold rolling or cold drawing.

Furthermore, the present invention enables stainless steels to be supplied as sheet, strip, foil or wire in a soft condition so as to facilitate severe forming into many different components, the composition of the steels being such that the components produced from them may be hardened uniformly across cold worked and non-cold worked parts and across welds of the same composition by heat treatment from relatively low temperatures with a minimum of scaling and distortion, to give a high tensile strength (over 65 tons/sq. in.), high yield point, low thermal expansion and after descaling, corrosion resistance of a high order.

Moreover, stainless steels according to the present invention, while securing the above mentioned advantages over well-known stainless steels, may yet, as an alternative, be capable of being supplied as flat rolled products or wire already heat treated to over 65 tons/sq. in. tensile strength.

Examples of the variable response to heat treatment according to composition are given in Tables I and II.

TABLE I.

Cast Analyses, %.

	Cast No.	C.	N_2.	Si.	Mn.	Cr.	Ni.	Cu.	Mo.	Ti.
A	01604	0.04	0.013	0.25	0.68	17.30	5.75	2.23	1.60	0.28
B	02216	0.04	0.012	0.40	0.74	16.80	5.74	2.25	1.69	0.26
C	03083	0.04	0.019	0.38	0.96	15.90	5.56	1.53	1.70	0.32
D	03427	0.03	0.022	0.30	0.84	16.40	5.57	2.23	1.63	0.30
E	03428	0.03	0.020	0.35	0.84	16.60	5.51	2.23	1.60	0.34
F	G6976	0.07	—	0.47	1.55	15.40	5.50	1.90	1.70	0.19
G	G6809	0.05	—	0.40	1.08	15.20	5.60	2.30	1.60	0.11
H	03930	0.04	0.023	0.24	1.07	15.90	5.63	1.78	1.75	0.07
J	06753	0.05	0.012	0.67	1.16	16.90	5.80	1.90	2.30	nil

TABLE II.

Response to Heat Treatment.

Treatment (1): Softened 20 minutes 1050° C. Air Cool (A.C.).
(2): Hardened (as above + 2 hrs. 700° C. A.C. + 2 hrs. min. 15° ÷ 2 hrs. 450° C. A.C.).

	Cast No.	Heat treatment.	0.5% P.S.	M.S.	El. %	
A	01604	(1)	21.4	49.8	33	
		(2)	69.0	71.5	22	
B	02216	(1)	24.2	53.6	29	
		(2)	70.0	73.8	16	
C	03083	(1)	46.4	64.0	13	(Inadequate softening)
		(2)	68.0	70.2	25	
D	03427	(1)	38.3	57.7	22	(Inadequate softening)
		(2)	79.8	82.5	20	
E	03428	(1)	32.2	57.7	21	(Inadequate softening)
		(2)	77.4	80.5	20	
F	G6976	(1)	18.7	56.0	36	
		(2)	75.0	78.6	22	
G	G6809	(1)	17.0	54.3	35	
		(2)	59.8	70.4	27	
H	03930	(1)	19.1	58.7	15	
		(2)	72.2	74.2	16	
J	06753	(1)	19.1	43.5	54	
		(2)	60.8	65.4	28	

Where the titanium content exceeds 0.30% the material does not fully respond to the softening treatment at 1050° C. Casts A to E inclusive are of the composition described in our above-mentioned earlier Patent Application. Of these, only casts A and B respond fully to the softening treatment. In all cases, however, a satisfactory response to the hardening treatment is noted.

Where the titanium content is less than 0.20%, as in casts F, G, H and J, the steel responds to both softening and hardening treatments.

In order to demonstrate that steels of similar composition to those described in our above-mentioned earlier Application, but without carbide stabilizing elements or with much smaller additions of these elements, are resistant to corrosion, tests were carried out on a steel of this type without titanium, cast 06753 (see Table I) in comparison with cast 01604 representing the composition described in the above-mentioned Application. Results are given in Table III.

TABLE III.

(1) Corrosion Tests in Sulphuric Acid.

Temp. °C.	Concentration (wt. % acid)	Weight losses in gms/cm.^{2}/24 hours. Cast 06753 (Steel J) 1050° C. A.C. + 2 hrs. 750° C. + 2 hrs. 450° C.	Cast 01604 (Steel A) 1050° C. A.C. + 2 hrs. 700° C. + 2 hrs. 450° C.
20	20	{0.0032 / 0.0000}	0.0013 / 0.0001
20	10	{0.0004 / 0.0000}	0.0001
20	5	{0.0000 / 0.0003}	0.0000
40	10	0.0003	0.0009
40	5	0.0001	0.0004
40	2.5	0.0001	0.0001

(2) Hatfield Boiling Copper Sulphate/Sulphuric Acid Test.

Cast 06753 (Steel J) 1050° C. A.C. + 2 hrs. 750° C. + 2 hrs. 450° C.	Cast 01604 (Steel A) 1050° C. A.C. + 2 hrs. 700° C. + 2 hrs. 450° C.
Unaffected	Unaffected

Experience has shown that martensitic stainless steels according to the present invention may be produced by conventional means in a variety of forms including castings, forgings, bar, wire, sheet and strip. They possess good casting properties and are easily hot worked. Moreover, when in the softened condition given by air cooling from 1050° C., they are readily cold rolled. cold drawn, formed or pressed. They may be subjected to a hardening treatment comprising maintaining the same to a temperature of from 700 to 800° C., for two hours, air-cooling to below 20° C., for example to 15° C., for at least two hours, and reheating to a temperature of from 350° to 600°, for example approximately 550° C., for from one to sixteen hours.

As an example of the way in which components may be produced from sheet steel of a composition within the present invention, supplied in the softened condition and subsequently heat treated from relatively low temperatures to a fairly uniform hardness throughout including both parts plastically deformed by cold working and other parts not plastically deformed, the following experiment was carried out :— 6" square blanks were cut from descaled sheet .080" thick in the softened condition after air cooling from 1050° C., and by a power spinning process were formed in one operation to give cones 3" deep and 4.25" inside diameter tapering to 1.25" inside diameter at the top. The wall thickness of the cones was .040" after spinning corresponding to a 50% reduction. An unworked flange at the wide end of the cones remained at the original sheet thickness of .080". Sections were cut across a cone in the cold worked condition and across similar cones heat treated, as shown below, and the following mean hardness readings were obtained (30 Kg. DHN) :—

Cold reduction.	As spun.	Treatment (a).	Treatment (b).	Treatment (c).
Nil (flange)	189	297	371	380
50% (cone walls)	417	304	340	366

Treatment (a) 2 hrs. 750° C. A.C.
Treatment (b) 2 hrs. 750° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C.
Treatment (c) 2 hrs. 800° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C.
A.C. = Air Cool.

It is advisable to cool to about 15° C. for at least 2 hours between the 700/800° C. hardening treatment and the secondary hardening treatment at 550° C.

A similar component produced from a non-heat treatable stainless steel of comparable corrosion resistance, e.g. an 18% chromium, 8% nickel steel, could not be obtained with the same uniformly high hardness and tensile strength across cold worked and non-cold worked parts. Such components could not, therefore, be used under the high applied stresses in service that are possible when using the steels described in this application.

A further advantage is obtained in components which have to be welded. It is possible to weld without peak hardening or cracking susceptibility. Uniform hardness, high yield and tensile strength are measured across such welds after the heat treatments described when the weld metal is of the same composition as the sheet or plate material. Typical tensile tests across welds of this type gave the following results :—

Tensile Tests across Argon Arc Welded Sheet 0.10" thick (weld at mid-gauge length.)

Heat treated as below, after welding :—

2 hrs. 700° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C. A.C.

	Yield point (YP)	Max. Stress (M.S.)	Elongation (El)	
1.	63.5	68.4	11% (2")	Broke ½" from weld
2.	64.2	68.0	10½% (2")	Broke ½" from weld

Moreover, cold rolled sheets or strips may be heat treated to high hardness of about 360 DHN in a manner similar to that described in the case of the spun cones with the advantages (a) that the high degree of flatness obtained by cold rolling may be retained through the use of hardening temperatures as low as 700° C., these being less liable to result in distortion than the higher hardening temperatures around 1000° C. used for some other martensitic stainless steels; and (b) cold rolled sheets heat treated in this manner show less directional properties, especially in terms of Young's Modulus, than cold rolled sheets without heat treatment and do not exhibit the Bauschinger effect when stressed in compression.

A variety of relatively low-temperature heat treatments of this type may be applied to modify or improve the properties of the cold rolled sheets in the manner indicated. Examples are given below along with the results of tensile tests carried out in the direction of rolling.

Condition or Heat Treatment.	0.1% P.S. tsi	M.S. tsi	El % (2"). %	Young's Modulus. tsi
(A) C.R. (20% reduction)	49.4	73.8	8	11500
(B) C.R. (20% reduction) + 1 min. 800° C. A.C.	22.9	68.0	11	— N.D.
(C) C.R. (20% reduction) + 1 min. 800° C. A.C. + 2 hrs. 450° C. A.C.	52.6	74.0	17	13050
(D) C.R. (20% reduction) + 10 mins. 750° C. A.C. + 4 hrs. 450° C. A.C. ..	75.2	79.2	7	12750
(E) C.R. (15% reduction) + 1 min. 830° C. A.C. + 2 hrs. – 10° C., + 2 hrs. 450° C. A.C.	70.7	79.3	16	— N.D.
(F) C.R. (33% reduction) + 1 min. 830° C. A.C. + 2 hrs. – 10° C., + 2 hrs. 450° C. A.C.	73.6	81.5	14	— N.D.

C.R. = Cold rolled. N.D. = Not determined.

Cold rolled sheets or strip supplied in the condition as heat treated for 1 to 10 minutes at 700/850° C., having mechanical properties similar to those shown by Test (B) above are amenable to mild stretch forming operations, the resulting components, or in the case of stretch flattening operations, the flattened sheet, may then be hardened with minimum risks of surface oxidation and distortion using a two-stage process consisting of cooling to about – 10° C. for 2 hours, followed by precipitation hardening, at any temperature in the range 350° C. to 600° C. for 1 to 16 hours, depending on the mechanical properties required in the finished component. The amount of cold reduction applied is not critical in regard to the mechanical properties of the finally heat treated sheet.

Alternatively, sheets or strips supplied in the softened condition after rapidly air cooling directly to room temperature may be hardened as follows :—

2 hours at a sub-zero temperature at or below – 78° C. followed by reheating to a temperature between 350° C. and 600° C. for periods of 1 to 16 hours.

Components hardened either by the sub-zero method or by the heat treatments previously described, have thermal expansion coefficients similar to those of well known steels such as 0.15% carbon, 16% chromium, 2% nickel steels. The following results have been obtained, being mean values over the temperature range specified :—

20—100° C.	..	0.0000119
20—200° C.	..	0.0000124
20—300° C.	..	0.0000128
20—400° C.	..	0.0000131
20—500° C.	..	0.0000133

The combination of properties provided by these steels, including suitability for double curvature forming and welding and the facility with which components produced from them may be uniformly hardened by means of relatively low temperature heat treatments applied after forming, giving high yields and tensile strength throughout, coupled with ferritic expansion and equivalent corrosion resistance to 18/8 steels, are of particular interest to the aircraft industry for structures based on strength/weight criteria.

We make no claim herein to any steel having a composition lying within the claims of our Specification No. 813,801.

WHAT WE CLAIM (SUBJECT TO THE FOREGOING DISCLAIMER) IS :—

1. Corrosion-resistant martensitic steel having a composition which is an improvement in or modification of the composition according to Patent Specification No. 813,801 and comprises :—

Carbon plus nitrogen	..	0.03 to 0.12%
with total nitrogen not exceeding 0.03%		
Chromium	..	over 13.5 and up to 17.5%
Nickel ..	..	4.0 to 6.0%
Copper	..	0.5 to 2.5%
Molybdenum ..	..	0.3 to 3.0%
Manganese	..	0.5 to 2.5%
Silicon ..	..	not more than 1%

0—0.2% of total content of any one or more of the following carbide- and nitride-forming elements, namely titanium, vanadium and niobium, and the remainder iron except for any aluminium introduced as an impurity in

ferro-alloys of the other constituents used, and small residual amounts of elements such as sulphur and phosphorus associated with steel-melting processes.

2. A corrosion-resistant martensitic steel as claimed in Claim 1, wherein the carbon content is not more than 0.06%, the chromium content 15 to 17%, the nickel content 5 to 6%, the copper content 1 to 2.5%, the molybdenum content 1.5 to 2.5%, and the content of the carbide- and nitride-forming elements consists of from 0.03 to 0.12% titanium.

3. A steel as claimed in Claim 1 or Claim 2, when cold-rolled and then subjected to a heat-treatment comprising heating for from 1 to 10 minutes at a temperature of from 700 to 850° C.

4. A steel as claimed in Claim 3 when hardened by a further treatment comprising cooling to approximately −10° C. for two hours, followed by precipitation hardening by maintaining at a temperature of from 350 to 660° C. for from 1 to 16 hours.

5. A steel as claimed in Claim 1 or Claim 2 which, in the softened condition resulting from rapid air cooling directly to room temperature from about 1050° C., is then subjected to a hardening treatment comprising maintaining the same at a temperature not above −78° C. for two hours, followed by heating to a temperature of from 350 to 600° C. for from 1 to 16 hours.

6. A steel as claimed in Claim 1 or Claim 2 which, in the softened condition resulting from rapid air cooling directly to room temperature from about 1050° C., is then subjected to a hardening treatment comprising maintaining the same to a temperature of from 700 to 800° C. for two hours, air-cooling to below 20° C., for example to 15° C., for at least two hours, and reheating to a temperature of from 350° to 600° C., for example approximately 550° C., for from one to sixteen hours.

7. A corrosion-resistant martensitic stainless steel having a composition substantially as described with reference to any one of Steels F, G, H and J in the foregoing Table I.

8. A steel as claimed in Claim 7 when subjected to any of the hardening treatments substantially as hereinbefore described.

BOULT, WADE & TENNANT,
111 and 112 Hatton Garden, London, E.C.1.
Chartered Patent Agents.

PROVISIONAL SPECIFICATION.

Improvements in or relating to Martensitic Stainless Steels.

We, John Ivan Morley, a British Subject, of 175 Hemsworth Road, Norton, Sheffield 8, Yorkshire, Charles Sykes, F.R.S., a British Subject, of Atlas & Norfolk Works, Sheffield 1, Yorkshire, and Robert Mowbray Norris Gray, a British Subject, of 10 Whirlow Park Road, Sheffield 11, Yorkshire, do hereby declare this invention to be described in the following statement:—

This invention relates to martensitic stainless steels possessing superior corrosion resistance and comprises an improvement in or modification of the steels described in our earlier Patent Application No. 26796/54 (Serial No. 813,801), hereinafter referred to as "the main Application."

The main Application described martensitic stainless steels composed of 0.03—0.15% carbon plus nitrogen (with total nitrogen not exceeding 0.05%) over 15% and up to 17.5% chromium, 4 to 6.5% nickel, 0.5 to 2.5% copper, 0.3 to 3.0% molybdenum, 1% maximum silicon, 1% maximum manganese together with one of the following carbide or nitride forming elements: niobium (including any residual tantalum) in amount between 8 and 12 times the carbon plus nitrogen content, titanium or vanadium in similar proportions whichever is used amounting to 5 to 10 times the carbon plus nitrogen content and the remainder substantially all iron except for any aluminium introduced incidentally as an impurity and small residual amounts of elements such as sulphur and phosphorus that are associated with steel melting processes.

Although steels within the above composition ranges may be hardened by heat treatment to give high proof stress and high tensile strength coupled with excellent corrosion resistance, they are not ideally suited to the production of flat rolled products by cold rolling, because individual casts vary in the degree of softening that may be achieved by air cooling the steels from about 1050° C. In some casts considerable amounts of austenite are retained by air cooling thin sections less than about $\frac{3}{16}$" thick from 1050° C. and the resulting yield points may be of the order 20 tons/sq. in. Such material may be fairly readily cold rolled to thin sheet or cold formed in the manufacture of components from sheet. Other casts, however, retain very little austenite after air cooling from 1050° C., and become martensitic after this treatment, with the result that they are hard and difficult to cold work. In both cases, however, the steels will respond to the subsequent hardening treatments described in the main Application.

In its broadest aspect, the present invention provides highly corrosion resistant

martensitic steels having a compositon consisting of 0.03 to 0.12% carbon plus nitrogen (with total nitrogen not exceeding 0.03%) over 13.5 and up to 17.5% chromium, 4.0 to 6.0% nickel, 0.5 to 2.5% copper, 0.3 to 3.0% molybdenum, 0.5 to 2.5% manganese, 1% maximum silicon, and up to 0.2% of any of the following carbide and nitride forming elements, titanium, vanadium or niobium and the remainder substantially all iron except for any aluminium introduced as an impurity in the ferro alloys, small residual amounts of elements such as sulphur and phosphorus associated with steel melting processes.

Steels according to the invention may be produced as castings, or as forgings, stampings, plates or bar by hot-rolling, or as cold-rolled sheet, strip, foil or cold-drawn wire, and may be heat-treated to a high tensile strength in a similar manner to that described in the main Application.

A preferred composition embodying the invention contains carbon not more than 0.06%, chromium 15% to 17%, nickel 5% to 6%, copper 1% to 2.5%, molybdenum 1.5% to 2.5% and titanium 0.03% to 0.12%.

The invention enables steels to be provided capable of being fully heat treated to develop mechanical properties and corrosion resistance similar to those according to the main Application and which by virtue of the slightly modified composition are capable of developing more consistently a soft low yield point condition as the result of an intermediate heat treatment, this property being advantageous in the production of sheet, strip, foil and wire rod or coil by the customary methods of cold rolling or cold drawing.

Furthermore, the present invention enables stainless steels to be supplied as sheet, strip, foil or wire in a soft condition so as to facilitate severe forming into many different components, the composition of the steels being such that the components produced from them may be hardened uniformly across cold worked and non-cold worked parts and across welds of the same composition by heat treatment from relatively low temperatures with a minimum of scaling and distortion, to give high tensile strength (over 65 tons/sq. in.), high yield point, low thermal expansion and after descaling, corrosion resistance of a high order.

Moreover, stainless steels according to the present invention, while securing the above mentioned advantages over well known stainless steels, may yet, as an alternative, be capable of being supplied as flat rolled products or wire already heat treated to over 65 tons/sq. in. tensile strength.

Examples of the variable response to heat treatment according to composition are given in Tables I and II.

TABLE I.

Cast Analyses, %.

	Cast No.	C.	N_2.	Si.	Mn.	Cr.	Ni.	Cu.	Mo.	Ti.
A	01604	0.04	0.013	0.25	0.68	17.30	5.75	2.23	1.60	0.28
B	02216	0.04	0.012	0.40	0.74	16.80	5.74	2.25	1.69	0.26
C	03083	0.04	0.019	0.38	0.96	15.90	5.56	1.53	1.70	0.32
D	03427	0.03	0.022	0.30	0.84	16.40	5.57	2.23	1.63	0.30
E	03428	0.03	0.020	0.35	0.84	16.60	5.51	2.23	1.60	0.34
F	G6976	0.07	—	0.47	1.55	15.40	5.50	1.90	1.70	0.19
G	G6809	0.05	—	0.40	1.08	15.20	5.60	2.30	1.60	0.11
H	03930	0.04	0.023	0.24	1.07	15.00	5.63	1.78	1.75	0.07
J	06753	0.05	0.012	0.67	1.16	16.90	5.80	1.90	2.30	nil

TABLE II.

Response to Heat Treatment.

Treatment (1): Softened 20 minutes 1050° C. Air Cool (A.C.).
(2): Hardened (as above + 2 hrs. 700° C. A.C. + 2 hrs. min. 15°C.+2 hrs. 450° C. A.C.)

	Cast No.	Heat treatment.	0.5% P.S.	M.S.	El. %	
A	01604	(1)	21.4	49.8	33	
		(2)	69.0	71.5	22	
B	02216	(1)	24.2	53.6	29	
		(2)	70.0	73.8	16	
C	03083	(1)	46.4	64.0	13	(Inadequate softening)
		(2)	68.0	70.2	25	
D	03427	(1)	38.3	57.7	22	(Inadequate softening)
		(2)	79.8	82.5	20	
E	03428	(1)	32.2	57.7	21	(Inadequate softening)
		(2)	77.4	80.5	20	
F	G6976	(1)	18.7	56.0	36	
		(2)	75.0	78.6	22	
G	G6809	(1)	17.0	54.3	35	
		(2)	59.8	70.4	27	
H	03930	(1)	19.1	58.7	15	
		(2)	72.2	74.2	16	
J	06753	(1)	19.1	43.5	54	
		(2)	60.8	65.4	28	

Where the titanium content exceeds 0.30% the material does not fully respond to the softening treatment at 1050° C. Casts A to E inclusive are of the composition described in Application 26796/54 (Serial No. 813,801). Of these only casts A and B respond fully to the softening treatment. In all cases, however, a satisfactory response to the hardening treatment is noted.

Where the titanium content is less than 0.20%, as in casts F, G, H and J, the steel responds to both softening and hardening treatments.

In order to demonstrate that steels of similar composition to those described in the main Application, but without carbide stabilizing elements or with much smaller additions of these elements, are resistant to corrosion, tests were carried out on a steel of this type without titanium, cast 06753 (see Table I) in comparison with cast 01604 representing the composition described in the above mentioned Application. Results are given in Table III.

TABLE III.

(1) Corrosion Tests in Sulphuric Acid.

Temp. °C.	Concentration (wt. % acid)	Weight losses in gms/cm.^{2}/24 hours. Cast 06753 1050° C. A.C. + 2 hrs. 750° C. + 2 hrs. 450° C.	Cast 01604 1050° C. A.C. + 2 hrs. 700° C. + 2 hrs. 450° C.
20	20	0.0032	0.0013
		0.0000	0.0001
20	10	0.0004	0.0001
		0.0000	
20	5	0.0000	0.0000
		0.0003	
40	10	0.0003	0.0009
40	5	0.0001	0.0004
40	2.5	0.0001	0.0001

(2) Hatfield Boiling Copper Sulphate/Sulphuric Acid Test.

Cast 06753 1050° C. A.C. + 2 hrs. 750° C. + 2 hrs. 450° C.	Cast 01604 1050° C. A.C. + 2 hrs. 700° C. + 2 hrs. 450° C.
Unaffected	Unaffected

Experience has shown that martensitic stainless steels according to the present invention may be produced by conventional means in a variety of forms including castings, forgings, bar, wire, sheet and strip. They possess good casting properties and are easily hot worked. Moreover, when in the softened condition given by air cooling from 1050° C., they are readily cold rolled, cold drawn, formed or pressed.

As an example of the way in which components may be produced from sheet steel of a composition within the present invention, supplied in the softened condition and subsequently heat treated from relatively low temperatures to a fairly uniform hardness throughout including both parts plastically deformed by cold working and other parts not plastically deformed, the following experiment was carried out:—6" square blanks were cut from sheet .080" thick in the A.C. 1050° C. softened and descaled condition and by a power spinning process were formed in one operation to give cones 3" deep and 4.25" inside diameter tapering to 1.25" inside diameter at the top. The wall thickness of the cones was .040" after spinning corresponding to a 50% reduction. An unworked flange at the wide end of the cones remained at the original sheet thickness of .080". Sections were cut across a cone in the cold worked condition and across similar cones heat treated, and the following mean hardness readings were obtained (30 Kg. DHN):—

Cold reduction.	As spun.	Treatment (a).	Treatment (b).	Treatment (c).
Nil (flange)	189	297	371	380
50% (cone walls)	417	304	340	366

Treatment (a) 2 hrs. 750° C. A.C.
Treatment (b) 2 hrs. 750° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C.
Treatment (c) 2 hrs. 800° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C.
A.C. = Air Cool.

It is advisable to cool to about 15° C. for at least 2 hours between the 700/800° C. hardening treatment and the secondary hardening treatment at 550° C.

A similar component produced from a non-heat treatable stainless steel of comparable corrosion resistance, e.g. an 18% chromium, 8% nickel steel, could not be obtained with the same uniformly high hardness and tensile strength across cold worked and non-cold worked parts. Such components could not, therefore, be used under the high applied stresses in service that are possible when using the steels described in this Application.

A further advantage is obtained in components which have to be welded. It is possible to weld without peak hardening or cracking susceptibility. Uniform hardness, high yield and tensile strength are measured across such welds after the heat treatments described when the weld metal is of the same composition as the sheet or plate material. Typical tensile tests across welds of this type gave the following results :—

Tensile Tests across Argon Arc Welded Sheet 0.10" thick (weld at mid-gauge length).

Heat treated as below, after welding :—

2 hrs. 700° C. A.C. + 2 hrs. 15° C. + 1 hr. 550° C. A.C.

1. 63.5 YP. 68.4 MS. 11% El. (2") Broke ½" from weld.
2. 64.2 YP. 68.0 MS. 10½% El. (2") Broke ½" from weld.

Moreover, cold rolled sheets or strips may be heat treated to high hardness of the order 360 DHN in a manner similar to that described in the case of the spun cones with the advantages (a) that the high degree of flatness obtained by cold rolling may be retained through the use of hardening temperatures as low as 700° C., these being less liable to result in distortion than the higher hardening temperatures around 1000° C. used for some other martensitic stainless steels; and (b) cold rolled sheets heat treated in this manner show less directional properties than cold rolled sheets without heat treatment.

Alternatively, sheets or strips supplied in the softened condition after rapidly air cooling directly to room temperature may be hardened as follows :—

2 hours at a sub zero temperature at or below − 78° C. followed by reheating to a temperature between 350° C. and 600° C. for periods of 1 to 16 hours.

Components hardened either by the sub zero method or by the double heat treatment previously described, viz. a preliminary hardening consisting of 2 hours 700/800° C. followed by air cooling to below 20° C. for at least 2 hours and finally reheating to a temperature between 350° C. and 600° C. for periods of 1 to 16 hours, have thermal expansion coefficients similar to those of well known steels such as 0.15% carbon, 16% chromium, 2% nickel steels. The following results have been obtained :—

20—100° C.	..	.0000119
20—200° C.	..	.0000124
20—300° C.	..	.0000128
20—400° C.	..	.0000131
20—500° C.	..	.0000133

The combination of properties provided by these steels, including suitability for severe double curvature forming and welding and the facility with which components produced from them may be uniformly hardened by means of relatively low temperature heat treatments applied after forming, giving high yields and tensile strength throughout, coupled with ferritic expansion and equivalent corrosion resistance to 18/8 steels, are of particular interest to the aircraft industry for structures based on strength weight criteria.

BOULT, WADE & TENNANT,
111 and 112 Hatton Garden, London, E.C.1.
Chartered Patent Agents.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1960.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2.